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JET ENGINE EXHAUST CHEMIION MEASUREMENTS: IMPLICATIONS FOR GASEOUS SO_3 AND H_2SO_4

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Abstract—We have made mass spectrometric measurements of negative chemiions (CI) in the exhaust of a jet engine on the ground. The measurements took place at plume ages between 6.6 and 19 ms at low- and high-fuel sulfur content (FSC). Total negative CI-number densities reached up to $1.4 \cdot 10^7$ cm^{-3} corresponding to an emission index for negative CI of 3×10^{15} CI per kg fuel. The most abundant negative CI species were found to be $HSO_4^- H_2SO_4$, $HSO_4^- SO_3$, $HSO_4^- HNO_3$, and $NO_3^- (HNO_3)_m$. Probably HSO_4^--containing ions are formed from NO_3^--containing ions by reactions with SO_3 and gaseous sulfuric acid (GSA). Hence our experiments indicate the presence of SO_3 and GSA. Building on this ion reaction scheme the S(VI) number density (S(VI) = $SO_3 + H_2SO_4$) was inferred from the CI-composition measurements. For low FSC one obtains (S(VI)) = 6.4×10^{11} cm^{-3} which corresponds to an efficiency for fuel sulfur conversion to gaseous S(VI) of $\varepsilon = 0.012$. Our findings have important implications for bimolecular H_2SO_4–H_2O-nucleation in jet aircraft exhaust plumes at cruise altitudes. New aerosol particles may form via homogeneous and/or CI-induced nucleation while heterogeneous nucleation on soot particles may activate soot particles to become water vapour condensation nuclei. Our findings imply that nucleation and condensational growth are more efficient than predicted by most previous models which assumed smaller ε.

Key word index: Jet exhaust ions, S(VI).

INTRODUCTION

Jet engines are thought to produce gaseous sulfuric acid (GSA) by oxidation of fuel sulfur to SO_3 and subsequent SO_3-conversion to GSA. This is indicated by recent experiments (*cf.* Reiner and Arnold, 1993; Frenzel and Arnold, 1994). Since GSA is a very efficient aerosol forming gas it may produce aerosol particles in jet aircraft exhaust plumes. GSA may undergo with H_2O bi-molecular nucleation and condensation leading to new particles (by homogeneous nucleation (HONU) and ion-induced nucleation (INU)) and to coated soot particles by heterogeneous nucleation (HENU) (*cf.* Hofmann and Rosen, 1978; Reiner and Arnold, 1993; Miake-Lye *et al.*, 1994; Kärcher *et al.*, 1995; Zhao and Turco, 1995; Brown *et al.*, 1996b). H_2SO_4–H_2O-nucleation may influence water contrail formation and thereby eventually even cirrus cloud formation.

Most critical parameters controlling H_2SO_4–H_2O-nucleation are the efficiency ε of fuel sulfur conversion to S(VI) ($=SO_3 + H_2SO_4$), the efficiency of SO_3-conversion to GSA in the very early exhaust plume, and plume dilution.

Previous laboratory experiments have revealed that CI formed in jet fuel combustion are sensitively influenced by GSA and that therefore these CI may serve as tracers for GSA-detection in the jet fuel combustion (Frenzel and Arnold, 1994). Recently, the first mass spectrometric measurements in the exhaust of modern large turbofan engines at the ground have been reported by Arnold *et al.* (1997). These measurements which took place in a test channel and at a plume age $t_p = 0.1$ s revealed the presence of cluster ions with HSO_4^-- and NO_3^--cores similar to the results of the laboratory burner experiments of Frenzel and Arnold (1994). The test channel experiments indicate $\varepsilon = 0.015$ and an emission index for negative CI of $E \geqslant 2 \times 10^{15}$ CI per kg fuel consumed. The test channel measurements do not indicate the presence of the GSA-precursor SO_3 which suggests that SO_3-conversion to GSA is completed already at $t_p < 0.1$ s.

The present paper reports on mass spectrometric measurements of negative CI in the exhaust of a small jet engine at the ground at very small plume ages between 6.6 and 14 ms. Here for the first time SO_3 was detected. Evidently at the very small plume

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ages SO_3-conversion to GSA is not yet completed. The present measurements indicate $\varepsilon = 0.012$ (only gaseous S(VI)) and an emission index for negative CI of $\geqslant 3 \times 10^{15}$ CI per kg fuel which are close to the values ($\varepsilon = 0.015$, $E \geqslant 2 \times 10^{15}$) obtained from the recent jet engine test channel measurements of Arnold *et al.* (1998).

EXPERIMENTAL

The present measurements of negative CI were made using a compact and automated ion mass spectrometer (IOMAS) which was built and operated by MPIK-Heidelberg. The measurements took place behind the research aircraft ATTAS (Advanced Technology Testing Aircraft System; type: VFW614 [*cf.* Busen and Schumann, 1995]) on the ground. Exhaust plume gas was sampled at a distance of 1.75 m downstream of the jet engine exit plane by a sampling tube (ST) which was fabricated from stainless steel and whose inner diameter was 4 cm. The conically shaped front section of the ST carried an inlet hole with a diameter of 0.3 cm. Pumping of the ST by a mechanical pump reduced the gas pressure inside the ST to a mean value of 30 hPa and induced a mean flow velocity of 36 m s^{-1}. At a distance of 2.8 m downstream of the sampling hole exhaust air and CI were sampled from the ST-flow through an inlet orifice (diameter: 0.02 cm) and entered the vacuum chamber of a quadrupole mass spectrometer (mass range 0–220 atomic mass units) which was pumped by a very efficient liquid-neon cooled cryopump. The mean CI-residence time in the ST was about 80 ms which markedly exceeds the ion residence time in the free plume (6.6–19 ms). However due to the low ST pressure (30 hPa) which is much lower compared to the free exhaust plume pressure (at least 1024 hPa; pressure ratio at most 0.029) chemical reactions, particularly the conversion of SO_3 to H_2SO_4 which involves two H_2O-molecules may not necessarily be more efficient in the ST compared to the free exhaust plume. A detailed description of the IOMAS-instrument can be found in Arnold *et al.* (1992) and Möhler *et al.* (1992).

CI-composition measurements were made for 4 power settings of the jet engine (type: RR M45H) and for two fuel sulfur contents (FSC = 0.212 g kg^{-1} and FSC = 2.68 g kg^{-1}). The power settings (PS in % of maximum PS) and the corresponding fuel consumptions (FC in g per s) were 7, 18, 30, and 57.7%, and 53, 99, 146 and 279 g s^{-1}, respectively. The sampling distance behind the jet engine exit plane was fixed at 1.75 m. Different FC corresponded to free exhaust plume flow velocities (v) and thereby different plume ages t_p of 19 ms ($v = 90$ m s^{-1}), 14 ms ($v = 125$ m s^{-1}), 10.5 ms ($v = 166$ m s^{-1}), and 6.6 ms ($v = 263$ m s^{-1}). As a tracer for exhaust gas, ΔCO_2 (excess CO_2 over "background" atmospheric CO_2) was measured using an infrared technique.

RESULTS AND DISCUSSION

Total count rates of negative CI were measured for different fuel consumption (FC) and are shown in Fig. 1 for a low fuel sulfur content (FSC = 0.212 g kg^{-1}) and in Fig. 2 for a high FSC (2.68 g kg^{-1}) with partial count-rates of individual CI-species. For low FSC total count-rates are around 1×10^4 s^{-1}. Considering a calibrated sensitivity of the ion mass spectrometer of up to $1.4 \cdot 10^7$ cm^{-3}, the above total count-rate corresponds to a negative ion number density $n^- = 1 \times 10^6$ cm^{-3} at the sampling point. Considering measured ΔCO_2 and a CO_2 emission index of 3160 g CO_2 per kg fuel corresponding to 4.3×10^{25} CO_2-molecules per kg fuel our above n^- corresponds to an effective emission index for negative CI of about $\geqslant 3 \times 10^{15}$ CI per kg fuel. For high FSC the total negative CI count rate is only 4000 s^{-1}. It is conceivable that here massive ions were abundant which fall outside the mass range of 220 amu of IOMAS. If so n^- would be underestimated for high FSC.

The measured negative CI composition is markedly different for the two different FSC which clearly indicates that fuel sulfur strongly influences negative CI. This was expected in the light of previous laboratory experiments with a jet fuel burner (Frenzel and Arnold, 1994). For low FSC the most abundant negative CI are $HSO_4^- HNO_3$, $HSO_4^- SO_3$ and $HSO_4^- H_2SO_4$. Besides these ions with HSO_4^--cores only traces of $NO_3^- (HNO_3)_m$ ions were present. Probably, the $NO_3^- (HNO_3)_m$ ions are initially formed and undergo conversion to $HSO_4^- (HNO_3)_m$ ions via reactions with GSA (*cf.* Frenzel and Arnold, 1994). Indeed the abundance ratio R_1 of ions with HSO_4^-- and NO_3^--cores increases with increasing plume age. However, even for the smallest plume age, R_1 is already much larger than one. This indicates that even for low FSC GSA was already abundant enough to convert most of the NO_3^--"cores". The first generation of product ions namely $NO_3^- (HNO_3)_m$ reacts with GSA and SO_3 leading to $HSO_4^- H_2SO_4$ and $HSO_4^- SO_3$ respectively. Hence $HSO_4^- SO_3$ indicates the presence of SO_3. This is reflected by the observed decrease of the abundance ratio $R_2 = (HSO_4^- SO_3 + HSO_4^- H_2SO_4)/HSO_4^- HNO_3$ with increasing plume age. Furthermore, the fractional abundance of $HSO_4^- SO_3$ decreases with increasing t_p which probably indicates a decrease of (SO_3) resulting from SO_3-conversion to GSA. However $HSO_4^- SO_3$ may also react with GSA leading to $HSO_4^- H_2SO_4$.

From R_1 and t_p the total concentration of gaseous S(VI) ($= H_2SO_4 + SO_3$) can be inferred using the expression:

$$[\mathrm{S(VI)}] = \ln(1 + R_1)/(kt_p) \qquad (1)$$

where k is the rate coefficient of the ion–molecule reaction which converts $NO_3^- (HNO_3)_m$ to $HSO_4^- (HNO_3)_m$ ions.

For $k = 1 \times 10^{-9}$ cm^3 s^{-1}, $t_p = 6.6$ ms and $R_1 = 65$ one obtains $[\mathrm{S(VI)}] = 6.4 \times 10^{11}$ cm^{-3}.

Considering the measured ΔCO_2 and the CO_2-emission index of 3160 g CO_2 per kg fuel (see above) the measured FSC = 0.212 gS per kg fuel leads to a total sulfur number density in the free plume of 5.2×10^{13} cm^{-3}. Hence our measured $[\mathrm{S(VI)}] = 6.4 \times 10^{11}$ cm^{-3} at $t_p = 6.6$ ms leads to $\varepsilon = 0.012$.

For high FSC (Fig. 2) only ions with HSO_4^--cores are present while ions with NO_3^--cores are virtually absent. Most likely this reflects much more efficient conversion of ions with NO_3^--core due to much larger S(VI)-concentrations (see below).

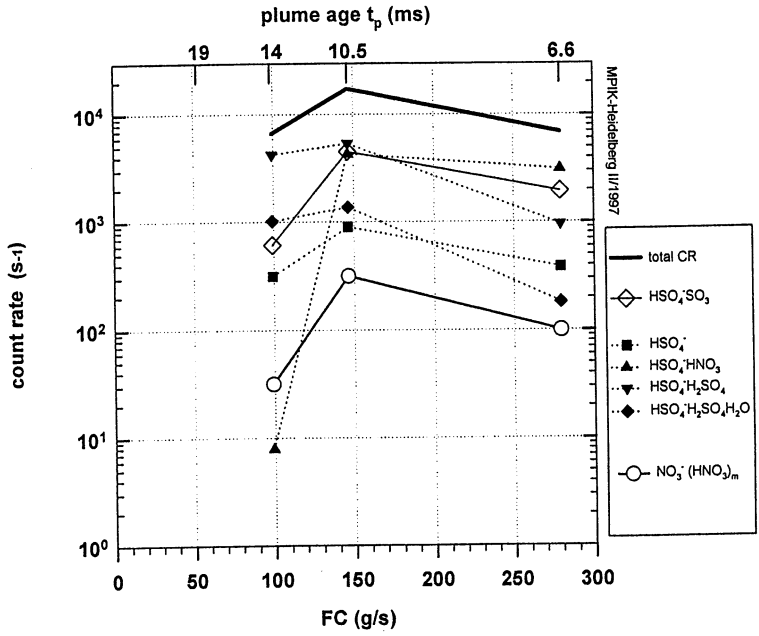

Fig. 1. Total and partial ion count rates of negative CI measured in the exhaust plume of a RR M45H jet engine at the ground as a function of fuel consumption (FC) and plume age (t_p). The fuel sulfur content was FSC = 0.212 g kg^{-1}.

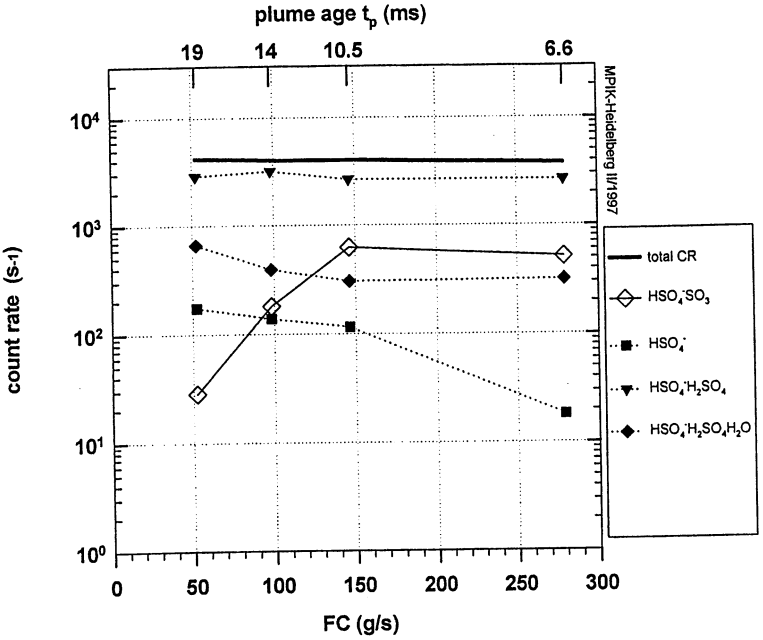

Fig. 2. As Fig. 1 but for FSC = 2.68 g kg^{-1}.

The abundance ratio H_2SO_4/SO_3 in the free exhaust plume cannot be inferred accurately from our data since it cannot be excluded that SO_3-conversion to H_2SO_4 may also take place in the sampling tube (ST). Note that the gas in the ST has a markedly lower temperature (360 K) and pressure (30 hPa) than the gas in the free plume. A lower temperature greatly increases while a lower pressure decreases the efficiency of SO_3-conversion to H_2SO_4. For $T = 360$ K the effective binary rate coefficient for the SO_3-reaction is 2.5×10^{-16} cm^3 s^{-1} (Kolb *et al.*, 1994; Lovejoy *et al.*, 1996) which leads to an SO_3-lifetime in the ST of only 266 ms. Considering a gas-residence time in the ST of 78 ms one finds that 25% of the initial SO_3

experiences conversion to H_2SO_4 which implies $H_2SO_4/SO_3 = 0.33$. Hence it is the strong negative temperature variation of SO_3-conversion to H_2SO_4 which makes this reaction important in the ST despite the low ST-pressure.

For low FSC and $t_p = 6.6$ ms the abundance ratio $HSO_4^- H_2SO_4/HSO_4^- SO_3$ is 0.5. If both ions are formed from $HSO_4^- HNO_3$ by reaction with H_2SO_4 and SO_3, respectively, and if the rate coefficients for these reactions are equal one obtains $H_2SO_4/SO_3 = 0.5$. This value is similar to the above ratio of 0.33 and therefore it cannot be excluded that the observed H_2SO_4 was indeed formed by SO_3 conversion in the ST. Note, however, that H_2SO_4 was unambiguously detected in the above-mentioned test-channel measurements and that there H_2SO_4 must have been formed in the exhaust plume. This is expected due to the high gas pressure and relatively low temperature in the free exhaust plume of the test-channel experiments. Also note that SO_3 will certainly become converted to H_2SO_4 in an exhaust plume at cruise altitude where temperatures rapidly fall to very low values. Within only about 1 s T falls to nearly ambient T which is around 230 K. This greatly increases the efficiency of SO_3-conversion to H_2SO_4 under cruise flight conditions.

Now the problem of missing CI indicated at high FSC will be investigated. For high FSC one expects $[S(VI)] \leqslant 1.1 \times 10^{13}\,cm^{-3}$ if ε would be the same as for low FSC ($\varepsilon = 0.012$). If so this would imply $\tau \geqslant 0.05$ ms (τ denotes the time constant of the H_2SO_4 reaction with ions) which is very much shorter than t_p. Hence ions of the type $HSO_4^- (H_2SO_4)_m$ with $m > 1$ may become abundant if they would not decompose thermally. Such ions have mass numbers of 293 ($m = 2$), 391 amu ($m = 2$) and more which exceed the mass range of the IOMAS instrument (220 amu). Therefore such ions with $m > 1$ would not have been detectable by IOMAS. This may indeed be the cause for smaller total CI-count rates measured for high FSC compared to low FSC.

SUMMARY AND CONCLUSIONS

The mass spectrometric CI-measurements reported here indicate a total negative ion concentration of up to $1.4 \cdot 10^7\,cm^{-3}$, an emission index for negative CI of about $\geqslant 3 \times 10^{15}$ CI per kg fuel. They also reveal the presence of $HSO_4^- H_2SO_4$, $HSO_4^- SO_3^-$ and $HSO_4^- HNO_3$ ions. The latter ions decrease with increasing plume age t_p and fuel sulfur content (FSC). Most likely, the observed ions are formed by conversion of $NO_3^- (HNO_3)_m$ ions via reactions with H_2SO_4 and SO_3. Building on this ion reaction scheme the total gaseous S(VI) concentration can be inferred from the CI composition measurements for low FSC ($0.21\,g\,kg^{-1}$). The resulting value is $(H_2SO_4 + SO_3) = 6.4 \times 10^{11}\,cm^{-3}$ which corresponds to an efficiency ε for fuel sulfur conversion to gaseous S(VI) of about 0.012 or 1.2%. This ε exceeds the most previously used values ($\varepsilon \approx 0.5\%$) (*cf.* Kärcher *et al.*, 1995; Miake–Lye, 1994) but is similar to most recent measurements by Arnold *et al.* (1997). Our measurements indicate the presence of SO_3 in the young exhaust plume. These findings of an efficient conversion of fuel sulfur to S(VI) have important implications for H_2SO_4-H_2O-nucleation in an exhaust plume at cruise altitude. Generally, they tend to increase the efficiencies for homogeneous nucleation and heterogeneous nucleation on soot. Finally, our measurements also indicate that ion-induced bi-molecular nucleation may be important (cf. Arnold *et al.*, 1997).

Future CI measurements at small plume ages should be made also for modern large turbofan engines which are typically used by wide-body jet airliners and under cruise altitude conditions. Furthermore, the mass range of CI-composition measurements should be increased.

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